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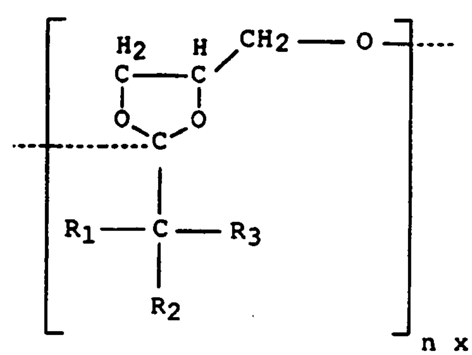
(54) Title: ADDUCTS OF GLYCIDYLESTERS OF ALPHA, ALPHA-BRANCHED CARBOXYLIC ACIDS AND CARBOXYLIC ACIDS AND POLY(ORTHO ESTER) AS INTERMEDIATE FOR THEIR PREPARATION



(I)

(57) Abstract: Poly(ortho ester) intermediate of general formula (I) wherein R_1, R_2 and R_3 are the same or different and each may represent an alkyl group containing from 1 to 10 carbon atoms and preferably from 1 to 6, wherein n represents an integer in the range of from 1 to 20 and preferably from 1 to 10; process for their preparation; adducts of glycidylesters and carboxylic acids and preferably acrylic acids, derived from said ortho esters; coating compositions comprising a binder component derived from said adducts.

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ADDUCTS OF GLYCIDYLESTERS OF α,α-BRANCHED CARBOXYLIC ACIDS AND CARBOXYLIC ACIDS AND POLY(ORTHO ESTER) AS INTERMEDIATE FOR THEIR PREPARATION

The invention relates to adducts of glycidylesters of α,α-branched carboxylic acids and carboxylic acids, to poly(ortho ester) as intermediate for their preparation and to a process for the preparation of solid poly(ortho ester) intermediates. These adducts are useful as constituent for binders in two component curable coating compositions and more in particular curable coating compositions for clear coat or coloured top coat for automotives or general metal coatings or industrial coatings.

Current trends in this coating market require faster curing formulations and one of the research efforts connected therewith was to change the mechanism of the oxirane ring opening, causing the formation of: fast-curing primary OH functional groups instead of the up-to-now occurring slow curing secondary OH group.

The incorporation of adducts of glycidylesters of α,α-branched carboxylic acids and e.g. acrylic acid into the (co)polymeric network obtained by radical copolymerization was known from e.g. R W Tess, "Epoxy Resins, Chemistry and Technology", C A May, Ed. 2nd, Marcel Dekker 1988, p 739, R S Bauer, Chem. Tech. (1980) 692 and British Patent No. 1285520.

On the other hand it was known from e.g. P Citovicky, V Chrastova, J Sedlar, J Beniska and J Mejzlik, Angew. Makromol. Chem. 171(1989) 141; M Zigon, U Osredkar and A Sebenik, J. Mol. Struct., 267(1992) 123; F B Alvey, J. Polym. Sci., Part A-1, 7(1969), 2117, Q Xie, R Liao,

D Wei and J Wang, Cuihua Xuebao, 3(1982) 303, Chem. Abstr. 98: 142917; S Doslop, V Vargha and F Horkay, Period. Polytech. Chem. Eng. 22(1978) 253; H Soler, V Cadiz and A Serra, Angew. Makromol. Chem. 152(1987) 55-60 Serra, V Cadiz, P Martinez and A Mantecon, Angew. Makromol. Chem. 138(1986) 185, that the 2-OH structure was the only compound or the predominant compound formed when reacting a variety of acids with the diglycidylethers and glycidylesters.

Therefore an object of the present invention was to provide modified adducts of glycidylesters of α,α-branched carboxylic acids containing in the acid moiety from 5 to 15 carbon atoms, and a carboxylic acid or an anhydride thereof, and which adducts contain predominantly primary OH groups.

Another object of the present invention was to provide a process for the preparation of said adducts in a reliable and controlled way.

Still another object of the present invention was to provide curable coating compositions which have been derived from said adducts aimed at, and show improved properties after application on in particular a metal carrier or substrate.

More in particular said object of the invention was to provide improved curable automotive top coat or clear coat compositions, comprising a copolymer derived from said adducts as one of the two components and a curing agent.

On the other hand, it was known for long that glycidylesters, when treated with Lewis acids, polymerize to form (substituted) polyethers. Whereas the older conception of using Al- and Zn-type of Lewis acids was confirmed in J C Ronda, A Serra and V Cadiz, Macromol. Chem. Phys. 200 (1999), 221, it was found by M Miyamoto,

Y Saeki, C W Lee, Y Kimura, H Maeda and K Tsutsui, Macromolecules, 30 (1997), 6067, that glycidyl acetate and methacrylate were converted into poly(ortho ester) when treated with methylaluminium Lewis acid. According to these authors the alternative polymerization pathway was due to the bulkiness of these specific catalysts. Therefore as the "normal" polymerization route of this present class of epoxy compounds (glycidylesters of branched acids) was regarded as the formation of polyethers and it was assumed that only in exceptional cases (strongly electron withdrawing substituent such as trifluoroacetyl or very bulky Lewis acids as catalyst) poly(ortho esters) could be formed.

As a result of extensive research and experimentation, such adducts aimed at could be surprisingly obtained.

Accordingly the invention relates to a process for the preparation of adducts of glycidylesters of α,α-branched carboxylic acids, having from 5 to 15 carbon atoms in the acid residue, and a carboxylic acid or anhydride thereof, and which adducts predominantly primary OH groups occur, comprising the oligomerization of the glycidylester into an ortho ester or poly(ortho ester), in the presence of a Lewis acid catalyst and/or a Brönsted acid (co)catalyst, and optionally in the presence of an apolar organic solvent, and subsequent conversion of said ortho ester or poly(ortho ester) with a carboxylic acid or anhydride into said adduct.

The process is preferably carried out under anhydrous conditions.

It will be appreciated that the invention also relates to the intermediate ortho esters or poly(ortho esters) and to the adducts themselves.

The carboxylic acids to be used for the preparation of the adduct from the intermediate ortho esters or poly(ortho esters) are preferably aliphatic or ethylenically unsaturated dicarboxylic acids, aromatic or cycloaliphatic mono-, di- or tri-carboxylic acids, or anhydrides thereof, or aliphatic branched monocarboxylic acids or ethylenically unsaturated monocarboxylic acids.

Suitable examples of ethylenically unsaturated mono- or di-carboxylic acids are acrylic acid, optionally substituted on the α carbon atom by an alkyl, aryl or cycloalkyl group, having from 1 to 6 carbon atoms and preferably alkyl having from 1 to 2 carbon atoms, and itaconic acid, maleic acid, fumaric acid.

Suitable examples of aromatic mono- or di-carboxylic acids are phthalic acid, terephthalic acid, isophthalic acid or anhydrides thereof, benzoic acid, p-tert.butyl benzoic acid, p-hydroxybenzoic acid, trimellitic acid, trimesic acid.

Suitable examples of aliphatic di-carboxylic acids are sebacic acid, glutaric acid, adipic acid, succinic acid, pimelic acid, α,α,α,α,-tetraalkylsubstituted pimelic acid, glutaric acid, adipic acid or succinic acid. Examples of cycloaliphatic carboxylic acids are hexahydrophthalic acid, hexahydrophthalic acids substituted by an alkyl group having from 1 to 4 carbon atoms and preferalby 1 or 2, such as methylhexahydrophthalic acid, ethylhexahydrophthalic acid, hydrogenated trimellitic acid, 1,4-cyclohexane dicarboxylic acid, the hydrogenated Diels Alder adduct of maleic anhydride with sorbic acid, or anhydrides thereof.

Examples of suitable aliphatic monocarboxylic acids are α,α-branched aliphatic monocarboxylic acids such as VERSATIC acids having from 5 to 20 carbon atoms in the acid moiety and preferably from 8 to 12 carbon atoms.

More preferred carboxylic acid reagents are acrylic acid, methacrylic acid, VERSATIC acids having 8 to 12 carbon atoms in the acid moiety, phthalic acid, phthalic anhydride, maleic acid, maleic anhydride, adipic acid, hexahydrophthalic acid or 1,4-cyclohexane dicarboxylic acid.

Most preferred are acrylic acid or methacrylic acid.

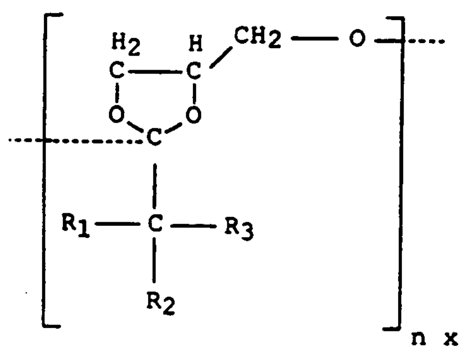
The oligomerization of the glycidylester into ortho ester or poly(ortho ester) and subsequent conversion of the ortho ester with a carboxylic acid into an adduct, predominantly containing primary OH groups, are preferably carried out in a solvent selected from toluene, xylene, and trifluorotoluene (TFT) and the like.

The process steps are preferably carried out under anhydrous conditions.

Depending on the specific starting glycidylesters of α,α-branched carboxylic acids, the temperature must be kept under a certain maximum in order to reach as much as possible primary OH groups in said adducts.

In the process of the present invention the temperature is kept at at most 100 °C and more preferably at at most 80 °C and most preferably at at most 60 °C.

Accordingly the invention relates to ortho ester or poly(ortho ester) intermediate of the general formula:



wherein R_1, R_2 and R_3 are the same or different and each may represent an alkyl group containing from 1 to 10 carbon atoms and preferably from 1 to 6, wherein n represents an integer in the range of from 1 to 20 and preferably from 5 to 10.

Preferred ortho ester or poly(ortho ester) intermediates are those wherein R_1, R_2 and R_3 are methyl groups and wherein n is in the range of from 7 to 10 and those wherein the sum of the carbon atoms in R_1, R_2 and R_3 is nine and wherein R_1 represents a methyl group, and n is in the range of from 7 to 10.

Preferred intermediate ortho ester or poly(ortho esters) are prepared from glycidylesters of α,α-branched acids containing 5 or 10 carbon atoms in the acid moiety, such as the commercial products CARDURA E5 or CARDURA E10, which are glycidylesters of pivalic acid and VERSATIC acid C10 (CARDURA and VERSATIC are trademarks).

In the process for the preparation of the poly(ortho ester) intermediates as defined before, a Lewis acid catalyst can be used selected from e.g. stannous octanoate, lithium triflate, stannous triflate, scandium triflate, borontrifluoride, chromo salene, titanium tetraisopropoxide, methyltrioxorhenium, ethylaluminium 2,2'-methylenebis(6-tert.butyl-4-methylphenoxide), methylaluminium-bis(2,5-di-tert.butyl-4-methylphenoxide), ethylaluminium-bis(2,6-di-tert.butyl-4-methylphenoxide), chloroaluminium-bis(2,6-di-tert.butyl-4-methylphenoxide), methylaluminium-2,2'-methylene-bis(6-tert.butyl-4-methylphenoxide), of which scandium triflate, stannous octoate, stannous triflate, methyltrioxorhenium, boron trifluoride-ethylether, lithium triflate and titanium tetra-isopropoxide are preferred.

The Lewis acid catalyst can optionally be combined with a Brönsted acid co-catalyst, depending on the

specific Lewis acid catalyst type or fully replaced by such Brönsted acid. The Brönsted acids may be selected from e.g. adipic acid, maleic acid, phthalic acid, trifluoracetic acid, or trifluoromethane sulfonic acid, of which the latter being preferred.

A clear preferred embodiment of the process is using triflic acid as cocatalyst, forming the ortho ester intermediate at temperatures in the range from 10 to 40 °C, within an acceptable time period.

It will be appreciated that the reactivity of the poly(ortho ester) is different from the original starting glycidylester and that it reacts with the selected carboxylic acid to give an adduct with a predominant proportion a primary hydroxyl group and is stable in the presence of base.

Moreover, depending on the present type of catalyst the poly(ortho ester) can be decomposed by water. Therefore their preparation has preferably to be carried out under anhydrous conditions.

Accordingly another aspect of the present invention is formed by adducts of glycidylesters of α,α-branched carboxylic acids, having from 5 to 15 carbon atoms in the acid residue, and a carboxylic acid, as specified hereinbefore, said adducts predominantly containing primary OH groups, and obtainable by reaction of ortho ester or poly(ortho ester) as specified hereinbefore, with a carboxylic acid, or anhydride thereof at a temperature of below a critical value dependent on the specific type of the starting glycidylester but in general below 100 °C and preferably below 90 °C. More in particular temperatures are in the range of from 90 to 40 °C and preferably from 50 to 70 °C.

For example the maximum temperature is 60 °C if the ortho ester has been derived from CARDURA E5

glycidylester and 90 °C if the ortho ester has been derived from CARDURA E10 glycidylester.

With the term "predominantly containing primary OH groups" as used throughout the present specification is meant that 50% or more of the total OH groups formed during the reaction of the poly(ortho ester) intermediate and an carboxylic acid and preferably acrylic acid, will be primary OH groups.

Preferably the fraction of primary OH groups will be at least 60%, and more preferably at least 80%.

More preferred are adducts, wherein the fraction of primary OH groups formed is at least 70% of the total number formed and preferably at least 80% of the total number formed.

It will be appreciated that another aspect of the present invention is formed by a process for the straight preparation of adducts, predominantly containing primary OH groups, via conversion of an ortho ester or a poly-(ortho ester) as specified hereinbefore with a carboxylic acid or anhydride thereof, without any isolation of said poly(ortho ester) at a temperature in the range of from 40 to 100 °C.

Another aspect of the present invention is formed by coating compositions, comprising at least a binder component and a liquid carrier, wherein the binder is a copolymer derived from one or more hereinbefore specified adducts as constituents, and optionally one or more additional comonomers having ethylenic unsaturation, by copolymerization by means of a radical initiator, and a cross-linker and a curing catalyst.

The binder copolymers used for coating compositions and in particular automotive coating compositions, have usually a total OH content (% m/m) in the range of from 3.10 to 3.25, a Mw in the range of from 3900 to 4200 and

Mw/Mn ratio in the range of from 1.4 to 1.8 and preferably from 1.5 to 1.7.

The viscosity (in mPa.s) of the copolymer solution at 60 wt% solids is usually in the range of from 180 to 320 at 22.5 °C. For example the maximum temperature is 60 °C if the ortho ester has been derived from CARDURA 5 esters and 95 °C if ortho ester has been derived from CARDURA 10.

Preferably these coating compositions comprise in addition a component, which is formed by a hydroxy-functional oligoether, derived from at least one polyol, free of carboxyl groups and having three or four hydroxyl groups and a monoglycidylester of an α,α-branched carboxylic acid containing from 5 to 15 carbon atoms.

More preferably said additional hydroxyfunctional oligoether applied, has a number average molecular weight Mn of from 150 to 1000, a molecular weight distribution MWD < 1.8 and a hydroxy value of between 180 and 700.

The coating compositions according to the present invention usually may contain one or more cross-linkers.

Many examples of such cross-linkers are commercially available as will be appreciated by those skilled in the coatings art. A preferred class of cross-linkers is formed by the polyisocyanate cross-linkers.

Various isocyanates employed as cross-linking agents are described in U.S. patent No. 4,322,508. However, the biuret or cyclotrimer of hexamethylene diisocyanate or isophorone diisocyanate are preferred.

Trifunctional isocyanates may be used, for example, triphenylmethane triisocyanate, 1,3,5-benzene tri-isocyanate, 2,4,6-toluene triisocyanate, an adduct of trimethylol and tetramethyl xylene diisocyanate sold under the trade name "Cythane 3160," "DESMODUR" N 3390 which is the timer of hexamethylene diisocyanate, and the

like (DESMODUR is a trademark). Optionally, one can use a polyisocyanate acrylic copolymer derived from isocyanatoethyl methacrylate (commercially available as TMI) and the like, as, for example, disclosed in U.S. patent 4,965,317 (col. 5).

As most preferred polyisocyanate cross-linker is used the cyclotrimer of hexamethylene diisocyanate.

Other film forming polymers, preferably in an amount of from 0 to 10 wt%, relative to the weight of the binder, may also be used in conjunction with the above-mentioned components. Other film-forming polymers may be linear or branched and may include acrylics, acrylo-urethanes, polyesters, polyester urethane, polyethers, and polyether urethanes that are compatible with the other components of the binder.

In addition, a coating composition according to the present invention may contain a variety of other optional ingredients, including pigments, pearlescent flakes, fillers, plasticizers, antioxidants, surfactants and flow control agents.

To improve weatherability of a finish produced by the present coating composition, an ultraviolet light stabilizer or a combination of ultraviolet light stabilizers can be added in the amount of about 0.1-3% by weight, based on the weight of the binder. Such stabilizers include ultraviolet light absorbers, screeners, quenchers, and specific hindered amine light stabilizers. Also, an antioxidant can be added, in the about 0.1-3% by weight, based on the weight of the binder.

Typical ultraviolet light stabilizers that are useful include benzophenones, triazoles, triazines, benzoates, hindered amines and mixtures thereof. Specific examples

of ultraviolet stabilizers are disclosed in U.S. patent No. 4,591,533.

The composition may also include conventional formulation additives such as flow control agents, for example, RESIFLOW S (polybutylacrylate) (RESIFLOW is a trademark), BYK 320 and 325 (high molecular weight polyacrylates)(BYK is a trademark); rheology control agents, such as fumed silica, microgels, and non-aqueous dispersion polymers; water scavengers such as tetrasilicate, trimethyl orthoformate, triethyl orthoformate, and the like.

When the present composition is used as a clearcoat (topcoat) over a pigmented colourcoat (basecoat) to provide a colourcoat/clearcoat finish, small amounts of pigment can be added to the clear coat to provide special colour or aesthetic effects such as tinting.

The present composition can be pigmented and used as the colourcoat, monocoat, primer, or primer surfacer. The composition has excellent adhesion to a variety of metallic or non-metallic substrates, such as previously painted substrates, cold rolled steel, phosphatized steel, and steel coated with conventional primers by electrodeposition. The present composition can also be used to coat plastic substrates such as polyester reinforced fibreglass, reaction injection-moulded urethanes and partially crystalline polyamides.

When the present coating composition is used as a basecoat, typical pigments that can be added to the composition include the flowing: metallic oxides such as titanium dioxide, zinc oxide, iron oxides of various colours, carbon black, filler pigments such as talc, china clay, barythes, carbonates, silicates and a wide variety of organic coloured pigments such as quina-cridones, copper phthalocyanines, perylenes, azo

pigments, indanthrone blues, carbazoles such as carbazole viote, isoindolinones, isoindolones, thioindioge reds, benzimidazolinones, metallic flake pigments such as aluminum flake and the like.

The pigments can be introduced into the coating composition by first forming a mill base or pigment dispersion with any of the afore-mentioned polymers used in the coating composition or with another compatible polymer or dispersant by conventional techniques, such as high speed mixing, sand grinding, ball milling, attritor grinding or two roll milling. The mill base is then blended with other constituents used in the coating composition to obtain the present coating compositions.

The coating composition can be applied by conventional techniques such as spraying, electrostatic spraying, dipping, brushing, flowcoating and the like. The preferred technique is spraying.

It will be appreciated that another aspect of the present invention is formed by cured coating composition layers on a carrier or support, the coating compositions comprising as binder a copolymer, wherein an adduct as defined hereinbefore is one of the constituents.

The present invention is illustrated by the following examples, however, without restricting its scope to these embodiments.

Example 1

At room temperature 5.0 g of CARDURA E5 glycidylester (32 mmol) and the selected catalyst (e.g. 121.5 mg stannous octoate) were intimately mixed and heated at the temperature listed in table 1, while stirring magnetically.

At specified intervals samples were drawn cooled to room temperature dissolved in $CDCl_3$, and analysed by ^1H-NMR and ^{13}C NMR spectroscopy. In some cases stirring

became impossible at high conversions of glycidyl pivalate, because of the increased viscosity.

When the general procedure was run at 60 °C for 5 days, all glycidyl pivalate had been converted (no residual epoxy groups detectable by NMR). The crude mixture was dissolved in chloroform and subjected to VPO-analysis (Vapour Phase Osmometry). The average number molecular weight was found to be 1263, indicating a degree of polymerisation of 8.7. The same sample was also subjected to SEC (Size Exclusion Chromatography) and showed an average number molecular weight of 1153 (EPIKOTE reference scale) and a molecular weight distribution Mw/Mn = 1.62.

The reaction mixtures derived from glycidyl pivalate were analysed by means of ^{1}H-NMR. The reaction products of CARDURA E5 consist of polyether (PE), poly(ortho ester) (POE), and the glycerol orthopivalate (OE). Each of the components exhibit very characteristic absorptions in the ^{1}H-NMR spectrum in $CDCl_3$ allowing the quantitative determination of the product composition.

The starting glycidyl pivalate showed characteristic peaks at 2.66, 2.86 and 3.22 ppm for the three protons in the vicinity of the epoxy group respectively.

The characteristic polyether (PE) proton was observed as a rather broad absorption at 5.1 ppm. The presence of a monomeric ortho ester (OE) was most clearly revealed by its ter.butyl absorption at 1.18 ppm or alternatively by the characteristic proton connected to the common carbon atom of the three monomeric orthopolyester rings, at 4.93 ppm. The poly(ortho ester) (POE) was characterized by its unique tert.butyl absorption at 1.00 ppm.

Table 1

Reaction of near CARDURA E5 glycidylester catalysed by $SnOct_2$ (1 mol %)

temp (°C)	time (h)	product (yield, %)[a]			GPC[b]	
		OE	POE	PE	Mn	Mw
60	24	0	56	tr		
60	120	0	99	tr	1153	1868
80	24	0	83	tr		
80[c]	96	0	93	tr		
80	72	tr	92	tr	1404	2130
80	96	tr	92	tr		
80[d]	144	0	98	tr		
100	25	tr	96	tr	871	1284
100	24	tr	95	tr		
100	48	tr	93	tr		
100	48	tr	100	tr		
120	24	tr	72	20	1159	1743
140	24	tr	60	40	1097	1529
	48	0	49	51		
	120	0	27	73		

a. tr=trace amounts; b. Epikote reference scale;
c. 0.01 mol% acrylic acid present; d. 1 mol% acrylic acid present.

The influence of solvents on the catalysed POE-formation is illustrated in Table 2.

Table 2

Solvent effect on $SnOct_2$ (1% molar) catalysed POE-formation from CARDURA E5 glycidylester

solvent	temp (°C)	time (h)	product (yield, %)[a]		
			OE	POE	PE
none	80	24	0	76	tr
		72	0	91	tr
toluene[b]	100	68	tr	25	tr
THF	65	24	8	25	tr
		72	tr	44	20
TFT	100	24	4	43	4
		72	7	53	10

a. tr=trace amounts; b. 30 mmol (5 g) Cardura in 10 g solvent.

The influence of different Lewis acids towards CARDURA E5 glycidylester and the reaction of neat CARDURA E5 glycidylester catalysed by various Lewis acids have been illustrated in Tables 3 and 4.

Table 3

Reactivity of different Lewis acids towards CARDURA E5 glycidylester

catalyst	moles (%)	temp (°C)	time (h)	CARDURA glycidyl-ester conversion (%)
$Sc(tf)_3$	0.1	25	1	32
$Bf_3.OEt_2$	0.1	25	1	30
$Sn(tf)_2$	0.1	25	20	26
$Sn(tf)_2$	1	25	2	53
$Sc(tf)_3$	1	100	1	100
Cr-salene	1	100	2	78
$SnOct_2$	1	100	2	64
$Ti(OiPr)_4$	1	100	2	33
MTO	1	100	2	21
$Sn(OAc)_2$	2	100	24	95
$SnOct_2$	2	100	24	89
$Sc(OAc)_3$	2	100	24	70
$Zn(OAc)_2$	2	100	24	45
Li(tf)	2	100	24	23

Table 4

Reaction of neat CARDURA E5 glycidylester catalysed by various Lewis acids

catalyst	moles (%)	temp (°C)	time (h)	product (yield, %) a			GPC[b]	
				OE	POE	PE	Mn	Mw
$SnOct_2$	1	100	25	tr	96	tr	871	1284
$SnOct_2$	0.8	100	4	5	80	15		
$SnOct_2$	0.1	120	24	tr	67	33	1159	1743
$Sn(tf)_2$	1	25	20	6	81	7	366	462
$Sc(tf)_3$	0.13	25	1	26	61	tr	358	728
$Sc(tf)_3$	0.07	25	8	9	59	5		
$Sc(tf)_3$	0.1	25	20	8	56	26		
Li(tf)	2	100	72	tr	100	0	2368	4316
TMStf	1	25	24	10	60	18		
$BF_3.OEt_2$	0.25	25	20	20	73	tr	365	421
$BF_3.OEt_2$	0.1	25	20	6	70	16	554	665
$BF_3.OEt_2$	1	25	1	9	70	8	1159	1743
$Ti(OiPr)_4$	1	100	24	tr	84	tr	1205	2284
MTO	1	100	24	6	59	20		
Cr-salene	1	100	2	56	22	tr		
$Sc(oAc)_3$	2	100	24	55	10	5		

$Sc(tf)_3$ = scandium triflate

$BF_3.OEt_2$ = boron trifluoride-diethylether

$Sn(tf)_2$ = stannous triflate

$Sn(tf)_3$ = stanni triflate

Cr-salene = chromic salene

$SnOct_2$ = stannous octoate

$Sc(oAc)_3$ = scandium acetate

$Ti(OiPr)_4$ = titanium isopropoxide

MTO = methyl trioxorhenium

$Sn(oAc)_2$ = stannous acetate

$Sn(oAc)_3$ = stanni acetate

$Zn(oAc)_2$ = zinc acetate

Li(tf) = lithium triflate

TMStf = trimethylsilyl trifluoromethanesulfonate

(B[DBMP]MA) = bis(2,5-di-tert.butyl-4-methylphenoxide) methyl aluminium

The Lewis acid catalysed reaction of CARDURA E5 in different solvents and the catalytic effect of Brönsted acids is illustrated in Tables 5 and 6.

Table 5

Lewis acid catalysed reaction of CARDURA E5 glycidylester in different solvents

solvent (conc)	catalyst (% m)	temp (°C)	time (h)	product (yield, %)[a]			GPC[b]	
				OE	POE	PE	Mn	Mw
none	$BF_3.OEt_2$ (0.25)	25	20	20	73	tr	365	421
toluene (1.5M)	$BF_3.OEt_2$ (1%)	25	24	29	71	tr		
none	$Sc(tf)_3$ (0.13%)	25	1	26	61	tr	358	728
toluene (5.2M)	$Sc(tf)_3$ (0.13%)	25	0.25	5	95	tr		
none	$Sc(tf)_3$ (0.07)	25	8	9	59	5		
TFT (2.5M)	$Sc(tf)_3$ (0.07%)	25	1	11	78	tr		
none	B[DBMP]MA (0.3%)	100	24	48	37	tr		
toluene (1.4M)	B[DBMP]MA (4%)	25	0.25	tr	100	tr	6280	19440

a. tr=trace amounts; b. Epikote reference scale

Table 6

Brönsted acids catalysed reaction of CARDURA E5 glycidylester

catalyst	moles (%)	temp (°C)	time (h)	product (yield, %)[a]		
				OE	POE	PE
acrylic acid	5	60	120	0	0	0
CF_3CO_2H	6	25	96	tr	6	tr
CF_3SO_3H	0.2	60	1	tr	54	30
CF_3SO_3H	1	25	18	18	55	18
CF_3SO_3H	0.5	25	4.5	25	50	10
			22	15	60	20

a. tr=trace amounts

The catalyst bis(2,5-ditert.butyl-4-methyl-phenoxide)methyl aluminium (B[DBMP]MA) used in Tables 5 and 6 was prepared by addition in portions of 1.10 g (5 mmol) of ditert.butyl-4-methylphenol to 1.25 ml of a 2M solution of trimethyl aluminium in toluene (2.5 mmol). The clear mixture was stirred for 20 hours at room temperature. Evaporation of the solvent gave B[DBMP]MA in almost quantitative yield and showing the following characteristics ^1H NMR ($CDCl_3$): 7.245 (s, 4H), 2.371 (s, 6H), 1.654 (s, 36H), -0.2 (s, 3H).

Example 2

Poly(ortho esters) of CARDURA E10 glycidylester were prepared under the conditions listed in Table 7.

Table 7

Reaction of neat CARDURA E10 glycidylester catalysed by various Lewis acids

catalyst	moles (%)	temp (°C)	time (h)	product (yield,%)[a]			GPC[b]	
				OE	POE	PE	Mn	Mw
$SnOct_2$	1	60	72	tr	26	tr		
$SnOct_2$	1	80	72	tr	34	51		
$SnOct_2$	1	100	48	0	26	51		
$Sn(tf)_2$	1	25	24	tr	71	20		
$Sc(tf)_3$	0.067	25	72	0	major	minor	508	573
Litf	2	100	72	tr	55	35		

Example 3(a)

The reactivity of the poly(ortho ester) of CARDURA E5 glycidylester with several selected reagents was tested in toluene, as depicted in Table 8.

Table 8

Reaction of the poly(ortho ester) of CARDURA E5 with some selected reagents in toluene[a]

catalyst used in preparation	reagent (molar ratio)	temp. (°C)	time (h)	conversion (%)	product
$SnOct_2$	acrylic acid (1)	60	20	93	18% 1-OH 75% 2-OH
$SnOct_2$	acrylic acid (2)	100	0.4	100	53% 1-OH 47% 2-OH
$SnOct_2$	acrylic acid (2)	100	0.75	87	47% 1-OH 40% 2-OH

Table 8 (cont'd)

catalyst used in preparation	reagent (molar ratio)	temp. (°C)	time (h)	conversion (%)	product
$SnOct_2$	benzoic acid (1)	100	0.17	86	85% 1-OH 15% 2-OH
$SnOct_2$	cyclo-hexane carboxylic acid (1)		0.40	85	75% 1-OH 25% 2-PH
Litf	acrylic acid (2)	100	0.25 1.5	100 100	>90% 1-OH 30% 1-OH 70% 2-OH
B[DBMP]MA	acrylic acid (0.6)	100	0.5	70^c	53% 1-OH 17% 2-OH
$SnOct_2$	p-tert.-butyl benzoic acid (2)	100	0.75	93	40% 1-OH 53% 2-OH
$SnOct_2$	H_2O (2)	100	1	0	
$SnOct_2$	H_2O (9)	100	84	100	glycerol pivalate
	CH_3CN/H_2O	25	20 175	0 82	glycerol pivalate (40% 1-, 60% 2-substituted)

Table 8 (cont'd)

catalyst used in preparation	reagent (molar ratio)	temp. (°C)	time (h)	conversion (%)	product
	standing in air[b]	25	100	100	glycerol pivalate (17% 1-, 83% 2-substituted)
	D_2O[b]	25	150	<30	
CF_3SO_3H	H_2O[b]	25	96	100	mainly PE no glycerol pivalate
CF_3SO_3H	standing in air[b]	25	1	100	>90% 1-substituted
$SnOct_2$	MeOH[d]	25	168	100	*
catalyst used in preparation	reagent (molar ratio)	temp. (°C)	time (h)	conversion (%)	product
$SnOct_2$	aniline (2)	100	3	0	

a. concentration about 1.0-1.5M; b. no solvent; c. no residual OE, 30% residual POE; d. about 1M solution in methanol

* poly(ortho ester) of CARDURA E5 glycidylester formed monoclyclic ortho ester, if dissolved in methanol; evaporation of the solvent led to the poly(ortho ester) again.

<u>Example 3b</u>

Adduct of acrylic acid and of CARDURA E10 glycidylester (ACE; 85 mole% 1-0 H isomer) was prepared (via the intermediate ortho ester) from a mixture of 24.6 g (100 mmol) of CARDURA E10 glycidylester, 100 ml of toluene, 7.92 g (110 mmol) of acrylic acid and 0.61 g (1.5 mmol) of Sn-octanoate. Said mixture was heated to 110 °C. After 5 hours the reaction mixture was evaporated. The yield was 30 g of ACE-adduct (100%, purity 86.5 by GC analysis and ^{1}HNMR. Said product (I) consisted of 85 mole% adduct isomer, containing a primary hydroxy group (1-OH isomer) and 15 mole% adduct isomer, containing a secundary hydroxy group (2-OH isomer).

Adduct of acrylic acid and CARDURA E10 glycidylester ACE (80 mole% 2-OH) was prepared by refluxing a solution of 505 mmol CARDURA E10 glycidylester, 500 mmol acrylic acid, 15 mmol EtPPI, 50 ppm (3.5 mg) of 4-ethoxyphenol and 400 ml of ter.-amyl-methylether at 80 °C during 24 hours, giving a yield of about 85%. After treatment of the cooled solution with 10 eg. AMBERLITE ion exchanger during 45 minutes at room temperature filtration, again treatment of the solution with AMBERLITE during 1 hour at room temperature, filtration and vacuum evaporation at room temperature, the 2-OH isomer was isolated in almost quantitative yield (product II) with a content of 2-OH isomer of 80 mol% and 1-OH isomer of 20 mole%.

The preformed ACE-adducts were copolymerized with other acrylic monomers to form an OH functional acrylic polymer resins I and II.

Into a round-bottomed glass reactor equipped with a stainless steel anchor stirrer, thermocouple and reflux condensor, the solvent was charged and heated until 140 °C. When the solvent reached said temperature, a mixture of the specific ACE adduct with the other comonomers and the initiator was added over a period of

4 hours followed by a post reaction of 2 hours with a supplement of initiator. The respective comonomer proportions and other details have been listed in the Table 9.

Table 9

	ingredients in parts weight
Initial reactor charge:	
Xylene	25
Monomer feed:	
ACE adduct I or II	58.5
Butylacrylate	6.5
Styrene	30
Methylmethacrylate	5
Di-tert.amylperoxide	4
Post-addition:	
Di-tert.amylperoxide	1

The resins obtained were evaluated by their final acid value, weight average molecular weight (Mw), molecular weight distribution (Mwd) and solids content.

The resins were first further diluted until 80% solids content with xylene and thereafter with butylacetate until 60% solids content to obtain the same solvent ratios.

At 60% solids content the coloud and viscosity was measured.

Table 10

	adduct resin I	adduct resin II
Polymer properties:		
Total OH content (%m/m)	3.18	3.18
Mw	4995	4156
Mw/Mn	1.7	1.54
Solution properties		
(at 60% solids):		
Viscosity (mPa.s)	309 at 22.4 °C	224 at 23.2 °C
Solids content (%w)	59.9	60.4
Colour (Pt/Co)	137.4	<20

Curing of resins

In order to evaluate the reactivity of the resins, blends with isocyanate curing agents and a cure catalyst were prepared. After application, the conversion was followed by decrease in isocyanate concentration as well as hardness development of the surface.

Details have been listed in Table 11.

Table 11

c) Copolymer resin of an adduct OH-1 (adduct resin I) — curing of the copolymer resin of adduct OH-1 adduct resin I

Time (hours)	Koenig hardness, heat cured	Time (hours)	Koenig hardness, ambient cured	Time (hours)	NCO (relative absorbance)
0.5	3	0.5	0	1	5.21
1	4	1	0	2.33	4.16
27	39	27	23	3	3.81
41.5	70	41.5	51	20.25	0.63
68.5	109	68.5	90	25.9	0.41
89.5	133	89.5	110	55.6	0.05
162.5	167	163	144		

e) Copolymer resin of an adduct OH-2 (adduct resin II) — curing of the copolymer resin of adduct OH-2 adduct resin II

Time (hours)	Koenig hardness, heat cured	Time (hours)	Koenig hardness, ambient cured	Time (hours)	NCO (relative absorbance)
0	0	0	0	1	5.20
1.5	0	2	0	2.33	4.36
20	14	20.5	10	3	4.10
26	17	26.75	15	20.25	1.90
68	51	140.5	63	25.9	1.60
141	72			55.6	0.60

Example 4

Adducts containing predominantly primary OH groups, of maleic acid or adipic acid, and of CARDURA E10 glycidylester, were prepared (via the intermediate ortho ester or poly(ortho ester) from a mixture 24.6 g (100 mmol) of CARDURA E10 glycidylester, 100 ml of toluene, 110 mmol of maleic acid or adipic acid (12.8 g and 16.2 g respectively), and 0.61 g (1.5 mmol) of Sn-octanoate or without any catalyst at all.

Said mixtures were heated to a temperature in the range of from 90 to 110 °C. The results and relevant reaction conditions have been listed in Table 12. After the indicated time periods, the reaction mixture was evaporated and the yield of the adduct, aimed at, was estimated via GC analysis and ^{1}H NMR.

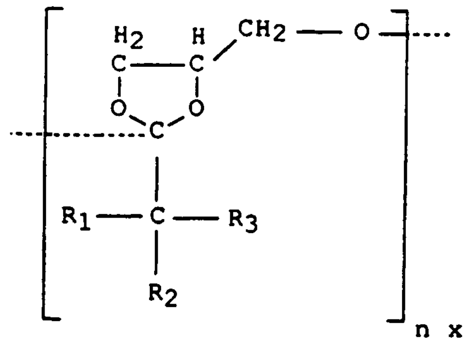
Table 12

Exp.	temp.	time		catalyst	prim. OH %
1	110 °C	30 m	CE + maleic acid	SnOct	69.30
2	110 °C	30 m	CE + adipic acid	SnOct	77.03
3	110 °C	1 hr	CE + adipic acid	SnOct	81.34
4	110 °C	30 m	CE + adipic acid	none	86.84
5	109 °C	3 h	CE + adipic acid	none	83.17
6	110 °C	5 h	CE + adipic acid	none	72.70
7	90 °C	30 m	CE + maleic acid	SnOct	78.89
8	90 °C	90 m	CE + maleic acid	SnOct	77.24

CE = CARDURA E10 glycidylester.

CLAIMS

1. Ortho ester or poly(ortho ester) intermediate of the general formula:

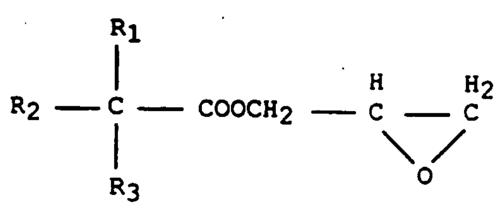


wherein R_1, R_2 and R_3 are the same or different and each may represent an alkyl group containing from 1 to 10 carbon atoms and preferably from 1 to 6, wherein n represents an integer in the range of from 1 to 20 and preferably from 1 to 10.

2. Ortho ester or poly(ortho ester) intermediate according to claim 1, wherein R_1, R_2 and R_3 are methyl groups and wherein n is in the range of from 1 to 10.

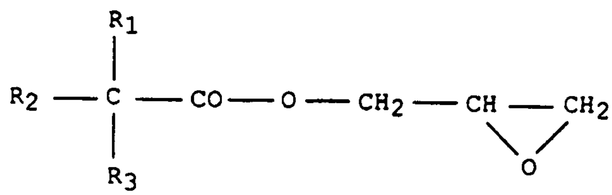
3. Ortho ester or poly(ortho ester) intermediate according to claim 1, wherein the sum of the carbon atoms in R_1, R_2 and R_3 is nine and wherein R_1 represents a methyl group, and n is in the range of from 7 to 10.

4. Ortho ester or poly(ortho ester) intermediate according to claim 1, obtainable by polymerization of glycidylesters of the formula:



wherein R_1, R_2 and R_3 are as defined hereinbefore, in the presence of at least a Lewis acid catalyst and/or Brönsted acid cocatalyst and optionally in the presence of an apolar organic solvent.

5. Process for the preparation of poly(ortho ester) intermediate according to claims 1-4, comprising the oligomerization of the glycidylester of an α,α-branched acid of the formula:



in the presence of a Lewis acid as catalyst and/or a Brönsted acid as cocatalyst and optionally in the presence of an apolar solvent at a temperature of at most 110 °C.

6. Process according to claim 5, characterized in that anhydrous conditions are used.

7. Process according to claim 5, characterized in that Sn octanoate is used as Lewis acid.

8. Process according to claim 5, characterized in that Sn triflate is used as Lewis acid at a temperature lower than 60 °C.

9. Process according to claim 5, characterized in that Li-triflate is used as Lewis acid at a temperature lower than 60 °C.

10. Process according to claim 5, characterized in that triflic acid is used as Brönsted acid catalyst at a polymerization temperature lower than 60 °C.

11. Adducts of glycidylesters of α,α-branched carboxylic acids, having from 5 to 15 carbon atoms in the acid residue, and a carboxylic acid or anhydride thereof, said adducts predominantly containing primary OH groups, and obtainable by reaction of poly(ortho ester) according to

claims 1-4, with a carboxylic acid, at a temperature of at most 110 °C and preferably at most 80 °C and more preferably in the range of from 50 to 70 °C.

12. Adducts of glycidylesters of α,α-branched carboxylic acids having 5 carbon atoms in the acid residue, and an aromatic carboxylic acid, ethylenically unsaturated carboxylic acid, a (cyclo)aliphatic carboxylic acid and preferably an acrylic acid optionally substituted on the α C-atom by an alkyl of from 1 to 4 carbon atoms, said adducts predominantly containing primary OH groups, and obtainable by reaction of an ortho ester or a poly(ortho ester) according to claim 2, with said carboxylic acid or an anhydride thereof, at a temperature of at most 60 °C.

13. Adducts of glycidylesters of α,α-branched carboxylic acids having 10 carbon atoms in the acid residue, and an aromatic carboxylic acid, ethylenically unsaturated carboxylic acid, a (cyclo)aliphatic carboxylic acid and preferably an acrylic acid optionally substituted on the α C-atom by an alkyl of from 1 to 4 carbon atoms, said adducts predominantly containing primary OH groups, and obtainable by reaction of an ortho ester or a poly(ortho ester) according to claim 2, with an optionally substituted acrylic acid at a temperature of at most 100 °C.

14. Adducts according to claim 11, characterized in that the fraction of primary OH groups is at least 60% of the total number OH groups formed.

15. Adducts according to claim 12, characterized in that the fraction of primary OH groups formed is at least 80% of the total number formed.

16. Process for the straight preparation of adducts, predominantly containing primary OH groups via conversion of a poly(ortho ester) according to claims 1-4 with a carboxylic acid or anhydride thereof, without any

isolation of said poly(ortho ester) at a temperature in the range of from 70 to 100 °C.

17. Coating compositions, comprising at least a binder component and a liquid carrier, wherein the binder is derived from one or more adducts according to claims 11-15, and optionally one or more additional comonomers, by copolymerization by means of a radical initiator, a cross-linker and a curing catalyst.

18. Coating compositions according to claim 17, characterized in that one of the additional components is formed by a hydroxyfunctional oligoether, derived from at least one polyol, free of carboxyl groups and having three or four hydroxyl groups and a monoglycidylester of an α,α-branched carboxylic acid containing from 5 to 15 carbon atoms.

19. Coating compositions according to claim 18, characterized in that the hydroxyfunctional oligoether applied, has a number average molecular weight Mn of from 150 to 1000, a molecular weight distribution MWD < 1.10 and a hydroxy value of between 180 and 700.

20. Cured coating composition of claims 17-19 applied on a carrier or support.

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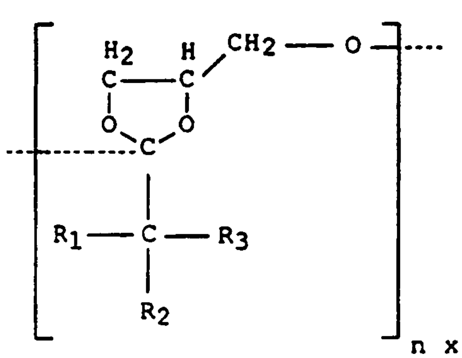
(54) Title: ADDUCTS OF GLYCIDYLESTERS OF ALPHA, ALPHA-BRANCHED CARBOXYLIC ACIDS AND ACRYLIC ACIDS AND POLY(ORTHO ESTER) AS INTERMEDIATE FOR THEIR PREPARATION



(I)

(57) Abstract: Poly(ortho ester) intermediate of general formula (I) wherein R_1, R_2 and R_3 are the same or different and each may represent an alkyl group containing from 1 to 10 carbon atoms and preferably from 1 to 6, wherein n represents an integer in the range of from 1 to 20 and preferably from 1 to 10; process for their preparation; adducts of glycidylesters and carboxylic acids and preferably acrylic acids, derived from said ortho esters; coating compositions comprising a binder component derived from said adducts.

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INTERNATIONAL SEARCH REPORT

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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data, BEILSTEIN Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	GELAS,J.: "Acétals cycliques dérivés de la glycérine. II. Synthèse et indication d'acétals hydroxylés et (ou) chlorés" BULL.SOC.CHIM.FR., 1970, pages 2341-2347, XP000882229 PARIS the whole document --- -/--	1,2,4,5

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
24 April 2001	04/05/2001

Name and mailing address of the ISA	Authorized officer
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Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Internal Application No
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